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FINAL TECHNICAL REPORT

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
on project entitled

PREPARATION AND PROPERTIES OF NEW INORGANIC GLASSES AND GEL-DERIVED SOLIDS

for

Grant No.: AFOSR 88-0066

Inclusive Dates: 1 November 1987 to 30 October 1990

Principal Investigator: John D. Mackenzie, Professor
Department of Materials Science and Engineering

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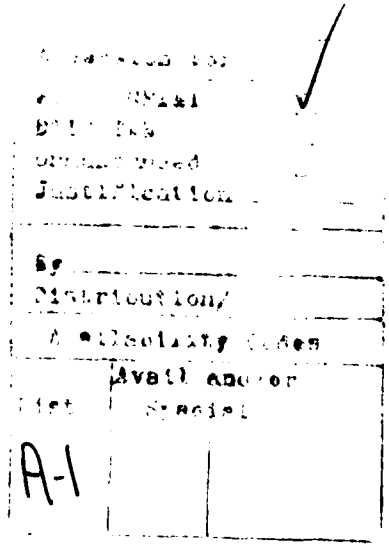
Research has been carried out on two families of solids. The first one involves solids made by the sol-gel process and includes composites. The second one involves non-oxide glasses based on fluorides, chalcogenides and chalcohalides. The structures of oxide gels were studied by X-ray photoelectron spectroscopy, liquid and solid state NMR. A new theory was developed on gel transformations. A number of new composites made by the sol-gel route were examined, including the use of SiC and diamond powder as fillers and some triphasic solids. Many ferroelectric thin films were prepared and their properties measured. An inorganic-organic gel material named "ORMOSIL" was developed which exhibited rubbery elasticity. The viscosity and viscoelasticity of fluorozirconate glasses and glass fibers have been studied. New chalcohalide glasses were prepared and their optical properties evaluated. Structural information was derived from Raman spectra. The interaction of UV radiation on chalcogenide fibers was investigated.

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ABSTRACT

Research has been carried out on two families of solids. The first one involves solids made by the sol-gel process and includes composites. The second one involves non-oxide glasses based on fluorides, chalcogenides and chalcohalides. The structures of oxide gels were studied by X-ray photoelectron spectroscopy, liquid and solid state NMR. A new theory was developed on gel transformations. A number of new composites made by the sol-gel route were examined, including the use of SiC and diamond powder as fillers and some triphasic solids. Many ferroelectric thin films were prepared and their properties measured. An inorganic-organic gel material named "ORMOSIL" was developed which exhibited rubbery elasticity. The viscosity and viscoelasticity of fluorozirconate glasses and glass fibers have been studied. New chalcohalide glasses were prepared and their optical properties evaluated. Structural information was derived from Raman spectra. The interaction of UV radiation on chalcogenide fibers was investigated.

1. Introduction

The current AFOSR-funded research program (Grant No. AFOSR-88-0066) at UCLA with Professor J.D. Mackenzie as Principal Investigator is concerned with investigations of two relatively new families of solids which are of importance to the U.S. Air Force. The program was started in November, 1987. The first family of materials consists of gel-derived solid oxides including glasses, crystalline ceramics and composites. The second family is concerned with non-oxide glasses which are infrared transmitting. The broad objectives of this program are to learn how to prepare these new solids via the understanding of chemistry and structures, measure some important properties and to correlate properties with structure, microstructure and chemical compositions. During these past three years a great deal of progress has been made with both types of solids. For instance, in the gel-derived materials area, superior ferroelectric thin films have been prepared and new "ORMOSILS" which exhibited rubbery behavior have been fabricated. In the non-oxide glass area, new chalcohalide glasses have been prepared and their structures elucidated. This progress was presented later in greater details.

This final technical report covers the period from 1 November 1987 to 31 October 1990.

2. Progress in Gel-Derived Solids Research

a. Ferroelectric Thin Films

The sol-gel method for the preparation of glasses and ceramics has a number of advantages over conventional methods.[1] One is the ability to achieve homogeneity at the molecular level since liquid molecules are mixed instead of micron-size powders. Another is the ease of fabrication of thin and thick films by dipping or spraying. A third one is the relatively low temperature of heat treatment to convert the amorphous gels into polycrystalline solids. Just prior to the commencement of this program, we were able to fabricate lead zirconium titanate (PZT) thick films which were transparent and which exhibited very good ferroelectric properties. Since the beginning of this program, we have been successful in fabricating many types of transparent ferroelectric thin films on a variety of substrates. Perhaps the most significant progress was made with single crystal silicon as substrates. Figures 1 and 2 illustrate the junction effects with PZT, lead barium niobate (PBN), $BaTiO_3$, strontium barium niobate (SBN) and $KNbO_3$. Details of ferroelectric properties are given in Table 1. This is the first time such behaviors have been reported. Another notable achievement is that we were able to lower the heat-treatment temperatures significantly and still obtain fully dense and transparent films. For instance, the heat-treatment temperatures for PZT was lowered from 700°C to 550°C

Preliminary experiments have been conducted to evaluate the applications of the sol-gel derived films in various potential devices. Figure 3 shows the photovoltaic behavior of PZT thin films. Figure 4

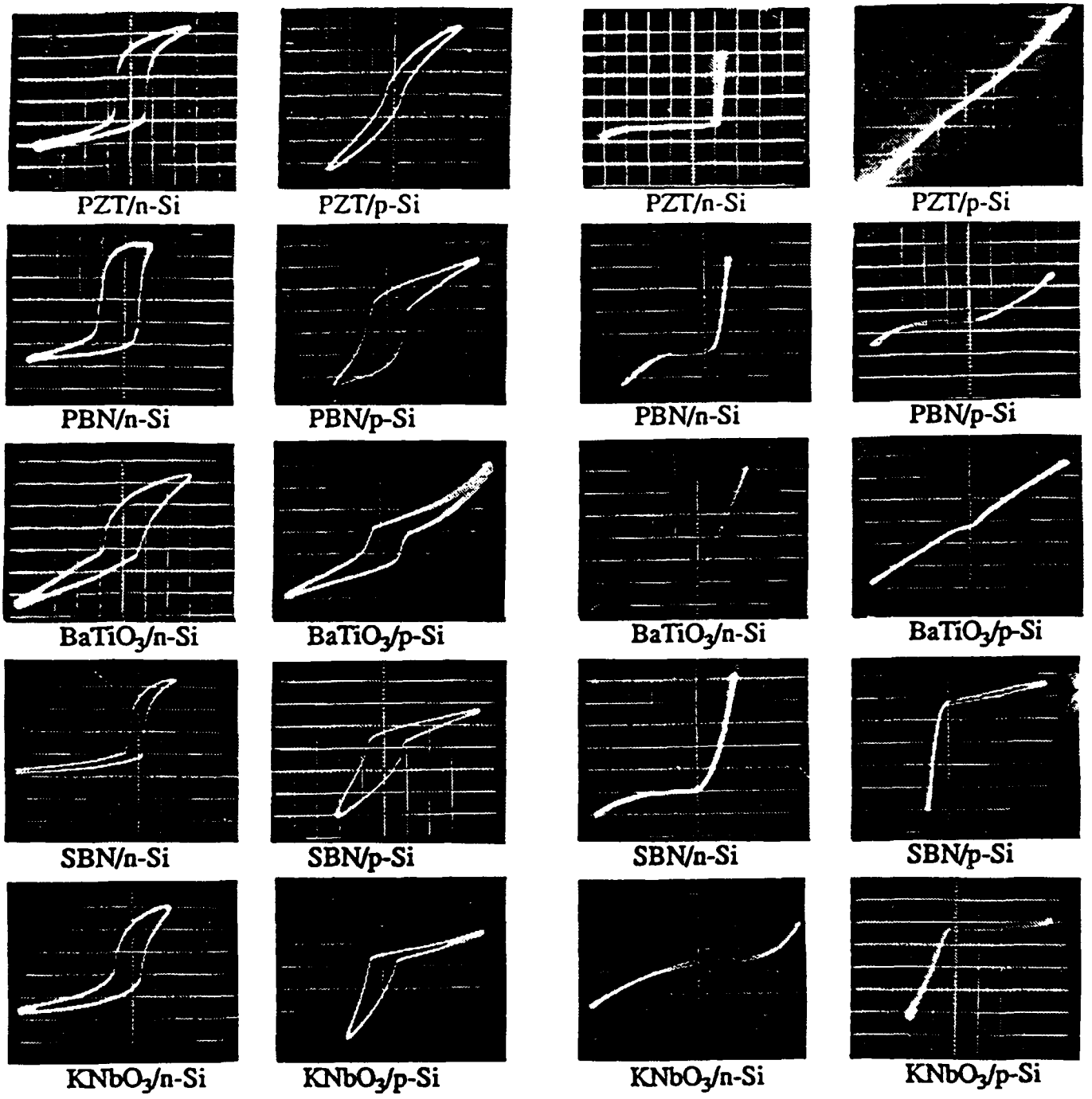
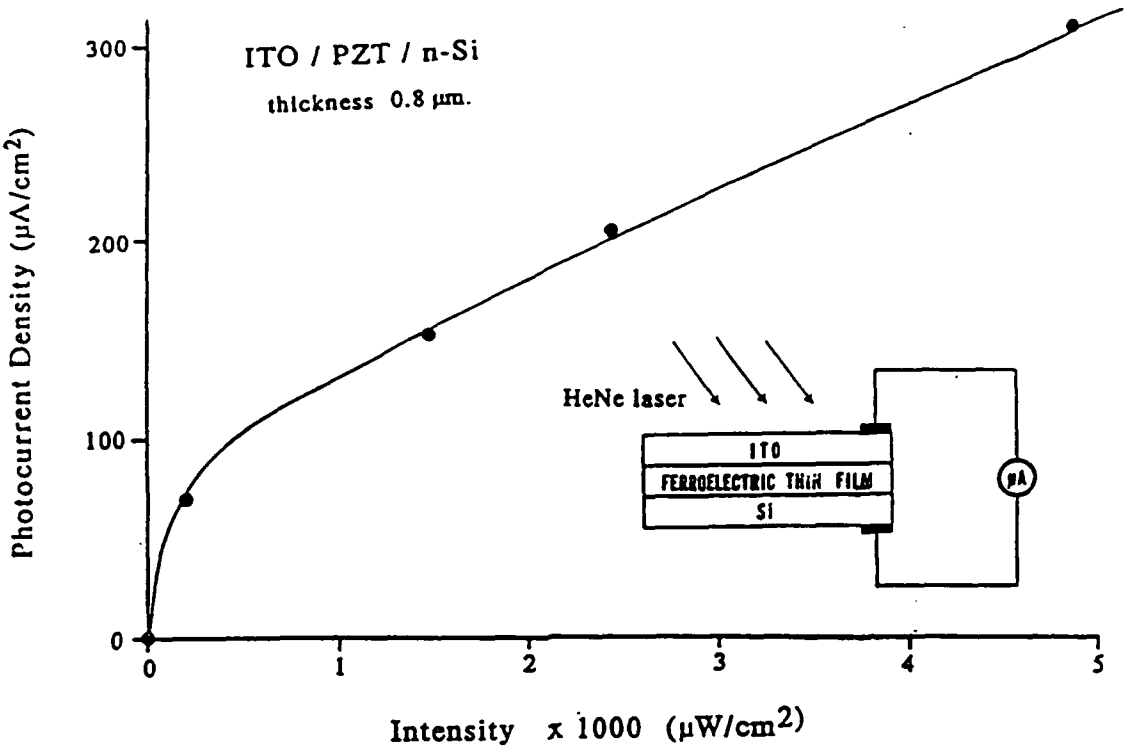


Fig. 1 P-E hysteresis loops of various ferroelectric thin films on semiconductive silicon wafers. (The scales per large division are referred to in Table 1.)

Fig. 2 I-V chracteristic curves (at 50 Hz) of various ferroelectric thin films on silicon substrates. (The scales per large division are referred to in Table 1.)



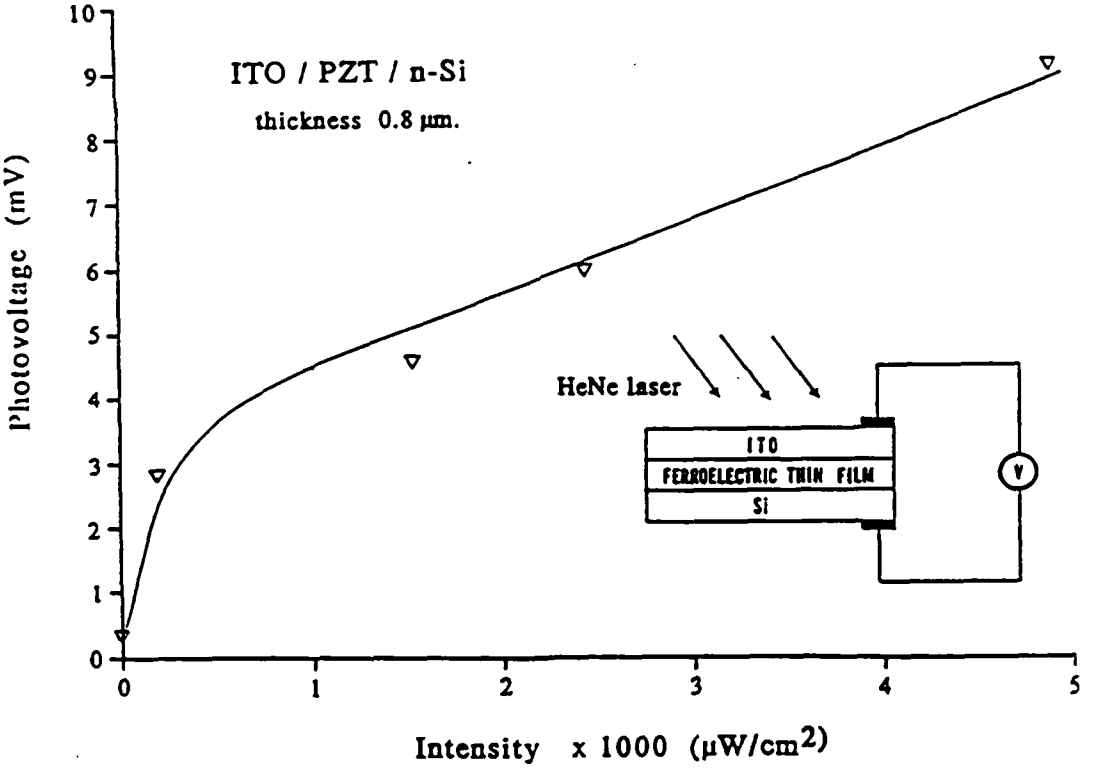
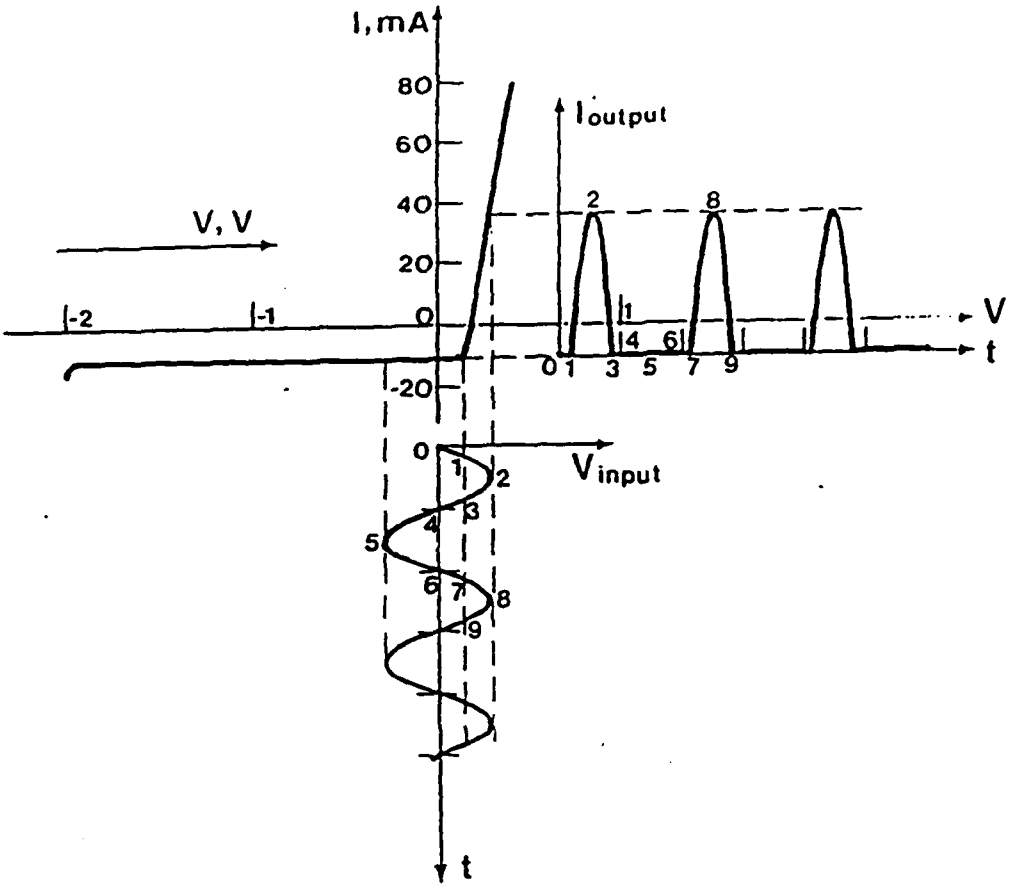


Fig. 3 Photovoltaic characteristics of PZT films on silicon.

Table 1. Ferroelectric properties obtianed from hysteresis loops at 50 Hz, capacitance, resistance, and I-V characteristics (50 Hz) of various ferroelectric films on silicon substrates at room temperature*

Ferroelectric Films	PZT		PBN		$BaTiO_3$		SBN		$KNbO_3$	
thickness (mm) substrates	0.8 n-Si	p-Si	1.1 n-Si	p-Si	0.8 n-Si	p-Si	v0.9 n-Si	p-Si	0.7 n-Si	p-Si
scale of x-axis of loop, field E (kkV/cm/div.)	22	24	3 6	81	112	144	85	86	143	136
scale of y-axis of loop, polarization P ($\mu C/cm^2$/div.)	18	13	15	14	16	8	22	17	9.5	8.9
remanent polarization P_R ($\mu C/cm^2$)	32	11	34	13	21	11	34	18	13	9
coercive field E_C (kV/cm)	15.7	9.6	32	65	83	86	51	68	86	81
capacitance (1 kHz, 1V) of F/S junction (pF)	105	106	107	110	97	110	103	104	99	101
dielectric loss 91 kHz, 1V) of F/S junction (%)	0.01	0.05	1.2	2.5	2.0	2	0.3	1.4	0.01	1.5
resistance, F/S junction (kΩ)	7x	8x								
(forward current 5μA)	10^4	10^4	6	12	10	13	10	50	50	50
resistance, F/S junction (MΩ) (reverse current 5μA)	> 300	> 300	5	0.06	20	0.09	20	3	10	20
scale of x-axis of I-V curve, V(V/div.)	1.5	0.43	5.6	7.8	5.6	6.2	14	11	7.3	13
scale of y-axis of I-V curve current density I($\mu A/cm^2$/div.)	12	4.6	7.5	7.5	15	5	15	23	29	13
$V_C + V^CD$, voltage when I = 0, (V)	1.5	0.17	4.5	11	5.0	2.5	15.6	-6.7	11.6	-13

* The electrode area on all of the films is 3.4×10^{-2} cm^2.



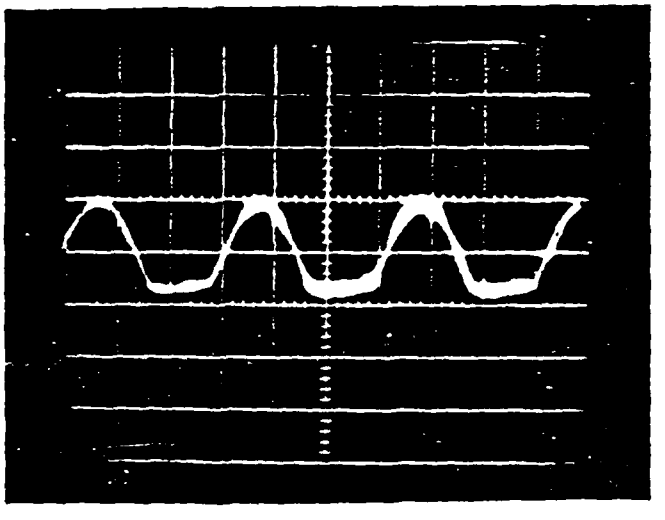


Fig. 4 A half-wave rectifier produces dc current from an ac voltage source (p-PZT on n-silicon)

shows the rectification property of PZT films also on silicon. A great deal of effort was also devoted to the investigations of SBN thin films on various substrates. The good optical property of a 0.8 mm thick SBN film on a silica glass substrate and its ferroelectric hysteresis loop is shown in Fig. 5. The pyroelectric coefficients of the SBN films were measured by a dynamic technique from 20° to 140°C. The results are shown in Fig. 6. The pyroelectric coefficient at 25°C was 2 x 10^{-8} C/cm^2K, approximately the same as that for SBN single crystals.[2] We have also successfully deposited SBN thin films on GaAs single crystal and obtained hysteresis loops of good quality. The many successes described above were possible because of the continuing study of the fundamental properties of sol-gel solutions, especially the relationship between solution structures and crystallization behavior. Most recently, we have been able to alter the microstructures of ferroelectric thin films by the application of an electric field during heat treatment.

Two patent applications have been submitted to the University of California Patent office on the above-mentioned work.

b. Rubbery ORMOSILS

ORMOSILS--organically modified silicates were first prepared by Schmidt.[3] Because sol-gel derived porous solids are both weak and brittle, densification to give dense oxides through heat-treatment is generally a difficult process. The porous gels can fracture easily on drying and heating. By the incorporation of long-chain organics which contain chain-terminating side groups, the brittleness of the normal three-dimensional gel structure would be reduced. For instance, polydimethyl siloxane (PDMS) can be incorporated into the three-dimensional network of Si-O bonds in a silica gel to increase the elasticity and hence to minimize cracking. Such materials have also been studied by Wilkes[4] and are named "Ceramers." Although the brittleness of such ORMOSILS has been shown to be significantly less than that of the oxide gels, no report of rubbery behavior has been published. Through systematic investigations of the various important factors which are known to have significant effects on the microstructure of gels, and the accumulated knowledge of the relationship between structure and properties, considerable progress has been made in our laboratory. Recently, we were able to prepare rubbery ORMOSILS based on PDMS and silicon alkoxides (TEOS, TMOS). Figure 7 shows the remarkable behavior of such an ormosil sample. No change on this rubbery behavior was observed even after 500 cycles of compression. Samples as large as 6" x 4" x 1" have been fabricated.

On heating to about 1000°C in an inert atmosphere (N_2 or Ar), the rubbery ORMOSILS became black porous solids, and the rubbery behavior was lost. Electron microscopic examinations revealed that carbon "islands" were trapped within SiO_2 cages. The black porous solids could be heated to 1400°C for many hours with no weight loss or shape change. Investigations into the potential applications of both

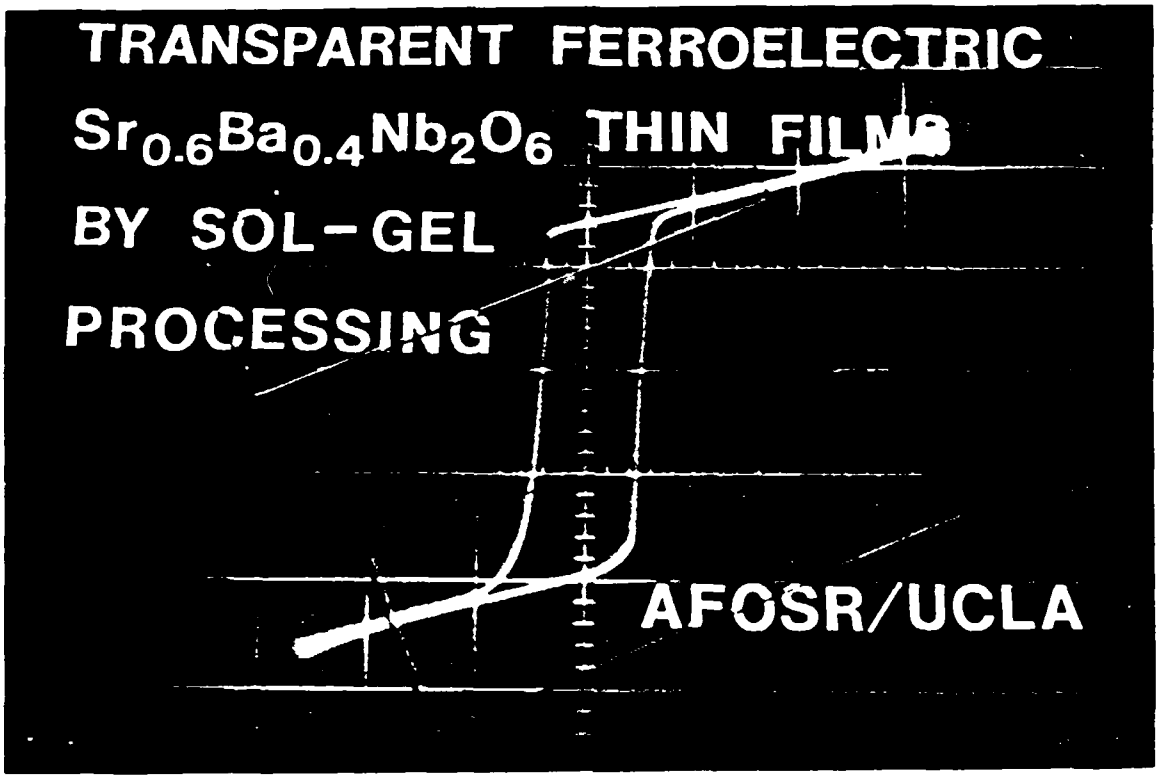


Fig. 5 Optically transparent SBN film on silica glass substrate and the hysteresis loop obtained.

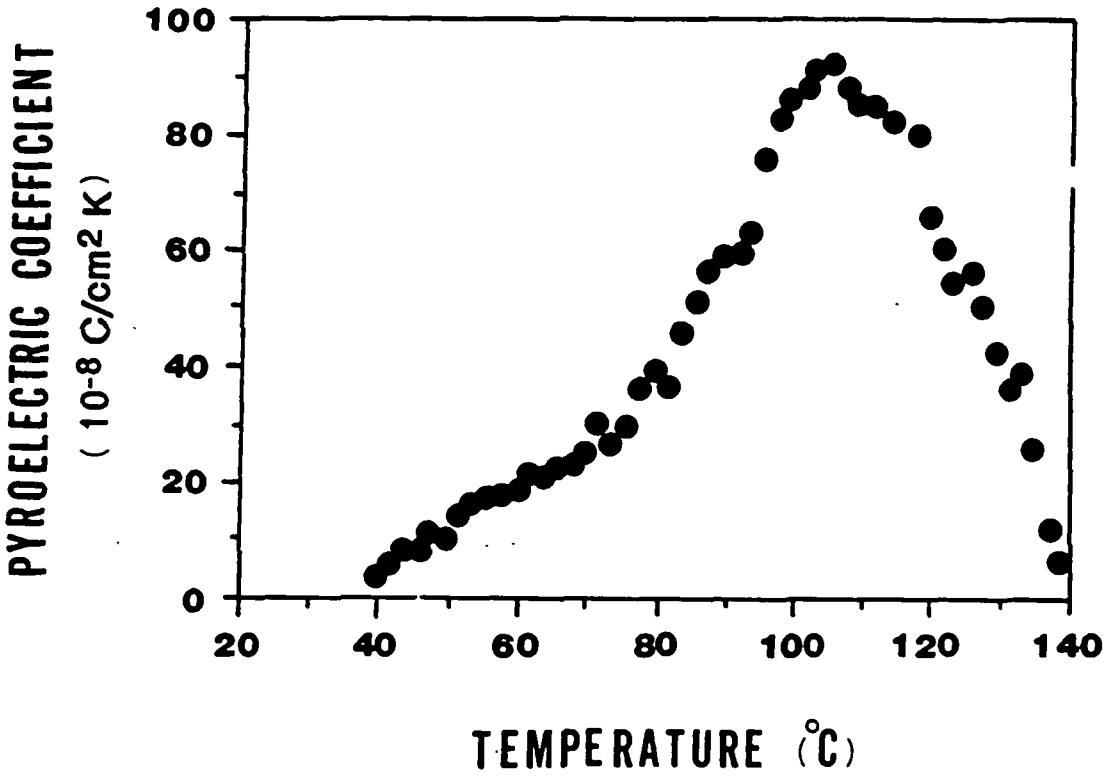


Fig. 6 Pyroelectric coefficients of SBN thin film from 40° to 140°.

the rubbery ORMOSILS and the black porous solids are in progress. Two patent applications have been submitted to the University of California Patent Office on the above-mentioned materials.

c. Ultrafine Particle Synthesis

An equipment was designed and constructed for the synthesis of ultrafine (< 0.1 mm) spherical particles of oxides from liquid solutions. Figure 8 shows the schematic diagram of the equipment. An ultrasonic vibrator was used to agitate liquid solutions and create mist particles. The mist particles were then transported by the passage of He gas up a vertical reaction chamber. The particles would lose liquid, decompose to give the spherical oxide particles, then collected. So far, $BaTiO_3$ and PbO spherical particles have been synthesized. In the case of $BaTiO_3$, alkoxide solutions in alcohols were used. For PbO, aqueous nitrate solutions were studied. A model has been formulated which offered satisfactory explanations of how the $PbNO_3$ decomposed to yield PbO. The ultrafine $BaTiO_3$ and PbO particles obtained are now being sintered in order to obtain transparent ceramics.

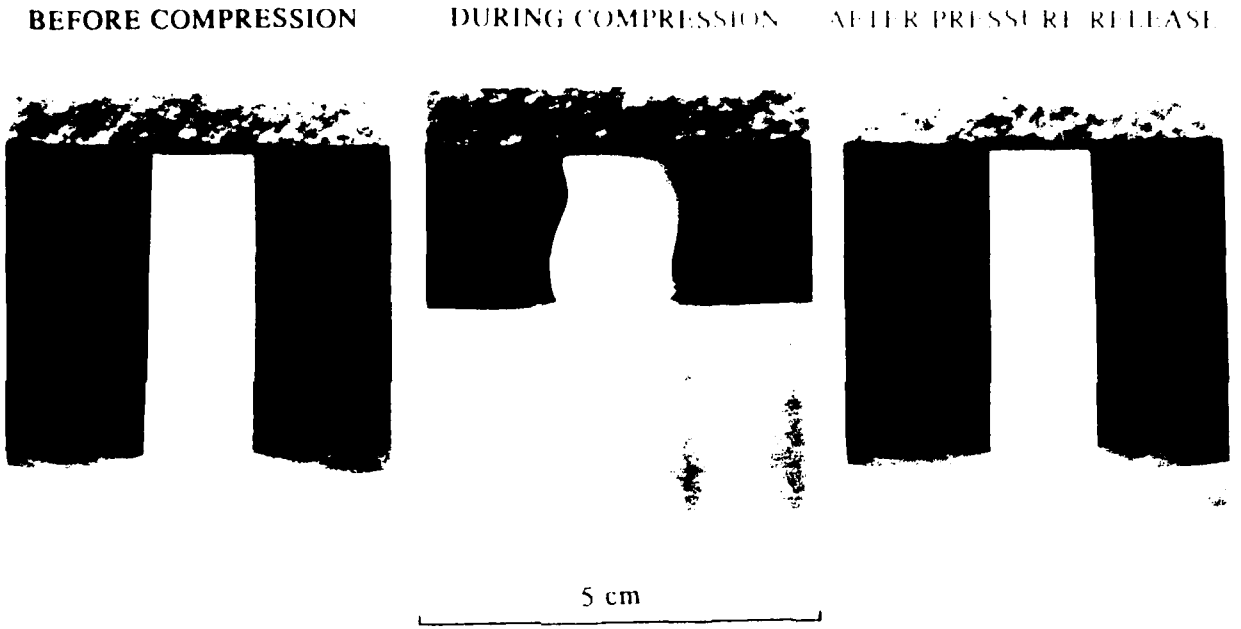
d. Fundamental Understanding of the Sol-Gel Process

The sol-gel process for the preparation of glasses and ceramics has received a great deal of attention in the past years.[5,6] Although this new processing route does hold promise for new materials and enhanced properties, truly successful applications are relatively few.[7] The main barrier to progress is the lack of sufficient knowledge on the process of gelation. The UCLA group has performed systematic studies on the effects of solvent, catalyst, raw materials and temperature on the rates of gelation, and the microstructure of the resulting gel. Silica was selected for the studies because of its relative simplicity. The very significant effects of all these factors were clearly demonstrated.[8]

We have started to investigate binary systems, especially silicates. Because so much is known on the structures and properties of binary alkali silicates, and because silicate glasses are known to exhibit the interesting "mixed-alkali effects," we selected the Li_2O-SiO_2 and K_2O-SiO_2 systems for investigations. Almost immediately, it was found that the two gel-forming systems exhibited methoxides. Figure 9 shows that the gelation times are very different. This is due to the higher apparent pH of the potassium system. The gelation process of the lithium system was followed with ^{29}Si NMR and ^{7}Li NMR. These studies show that the polymerization of the TMOS to form gel is accompanied by the de-polymerization effects of the Li ions, somewhat similar to the network modifying effects of alkali ions in silicate glasses. A study of the structures of dried gels was made with ^{29}Si MAS-NMR.

Figure 10 shows a comparison of the two systems. The spectra are clearly very different for the high alkali gels. These results show that the dried gel structures also are very different from those of the alkali silicate glasses. They are in support of our previous studies on non-bridging oxygen ions in Na_2O-LiO_2 gels.[9]

RUBBERY BEHAVIOR OF GEL



ε_{comp} = 68%

E_{comp} = 2.66 Mpa

σ_{comp} = 12.5 Mpa

Fig. 7 Rubbery Behavior of Gel

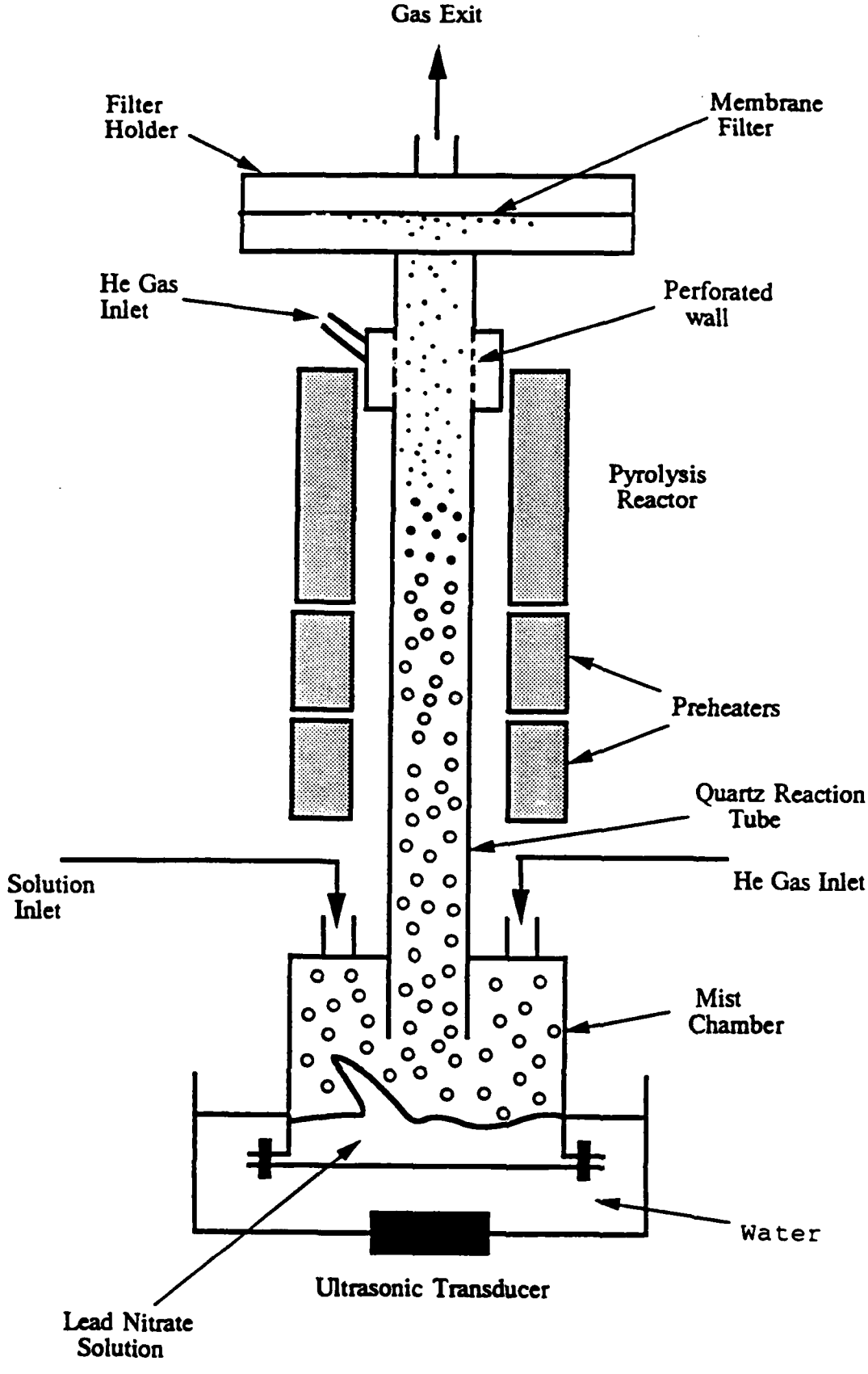


Fig. 8. Schematic diagram of experimental systems.

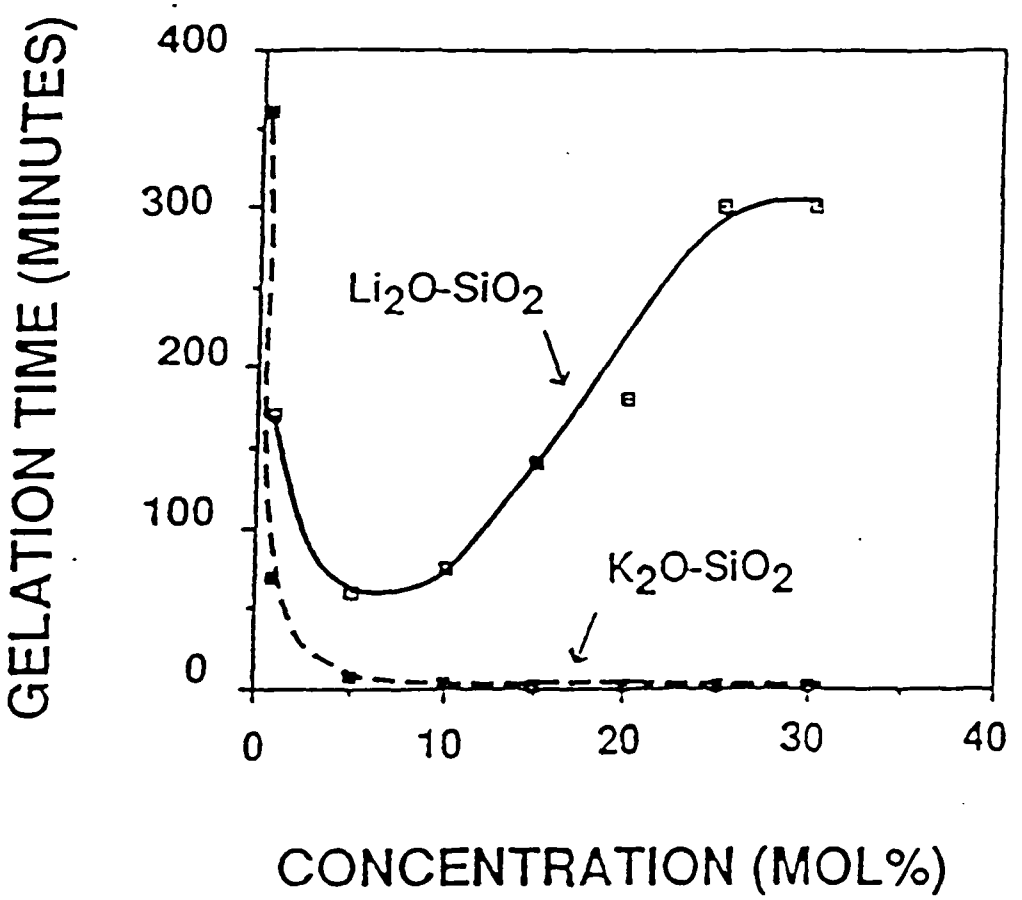


Fig. 9 Evolution of the gelation times with the alkali content in the Li_2O-SiO_2 and K_2O-SiO_2 systems.

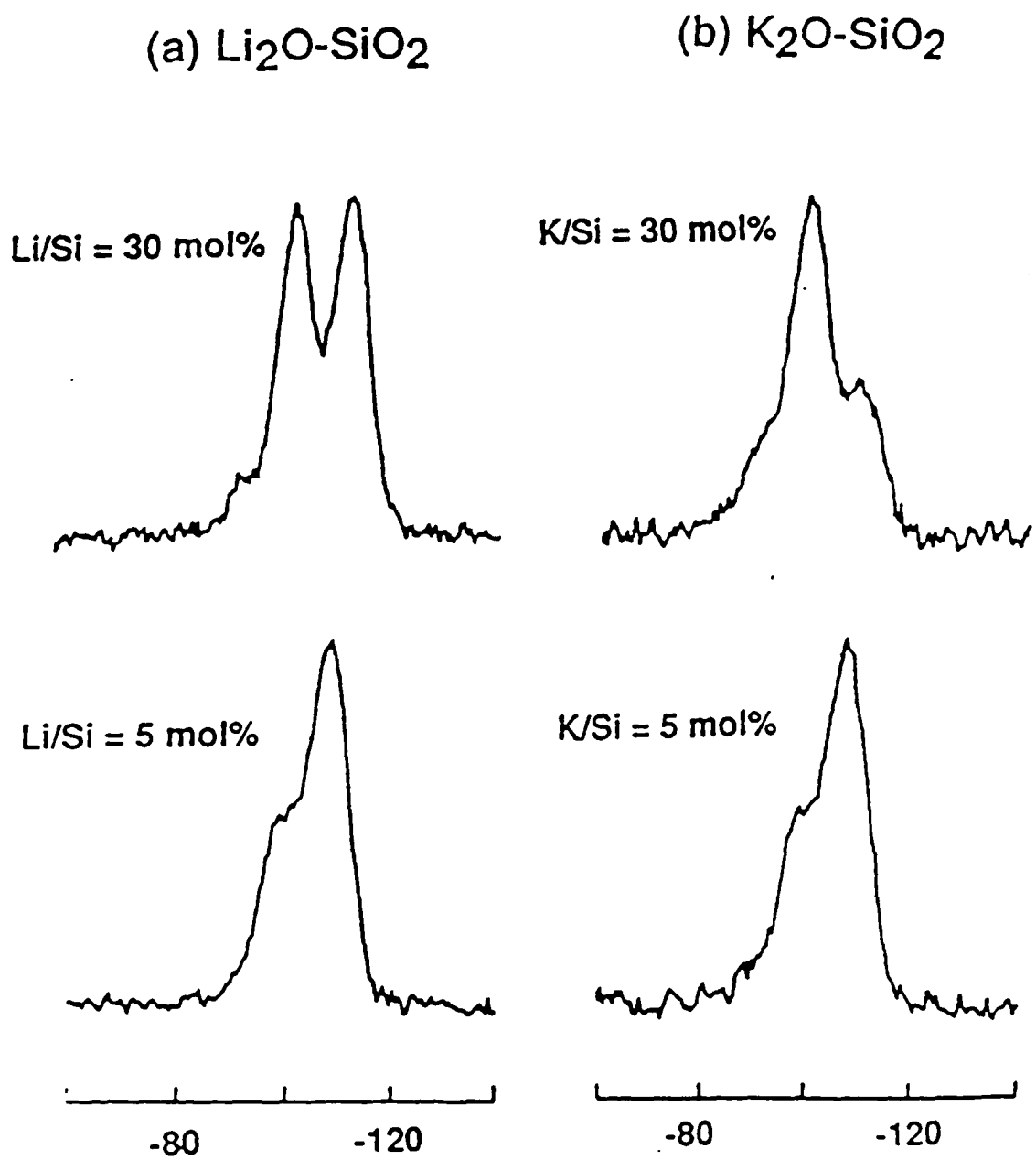


Fig. 10 Evolution of ^{29}Si MAS-NMR spectra of dried gels in the Li_2O-SiO_2(a) and K_2O-SiO_2(b) systems.

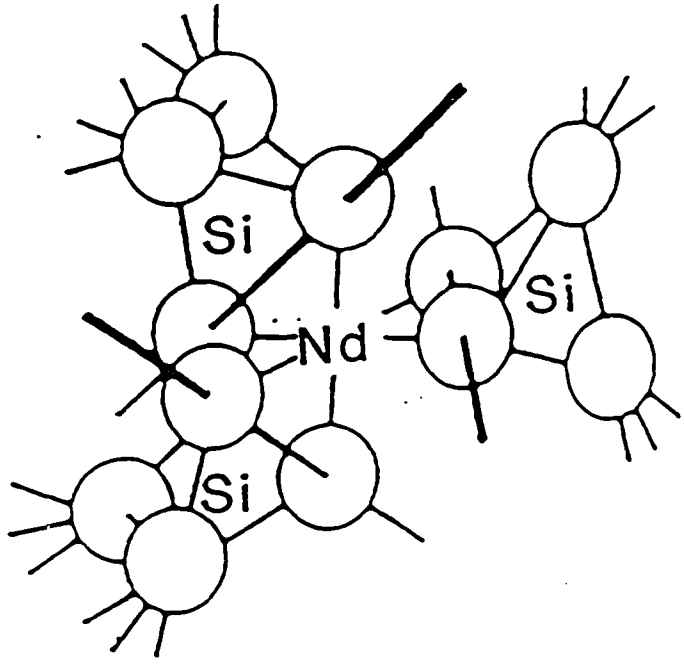


Fig. 11. Proposed local environment of Nd ion in SiO_2 glass at low concentrations of Nd_2O_3.

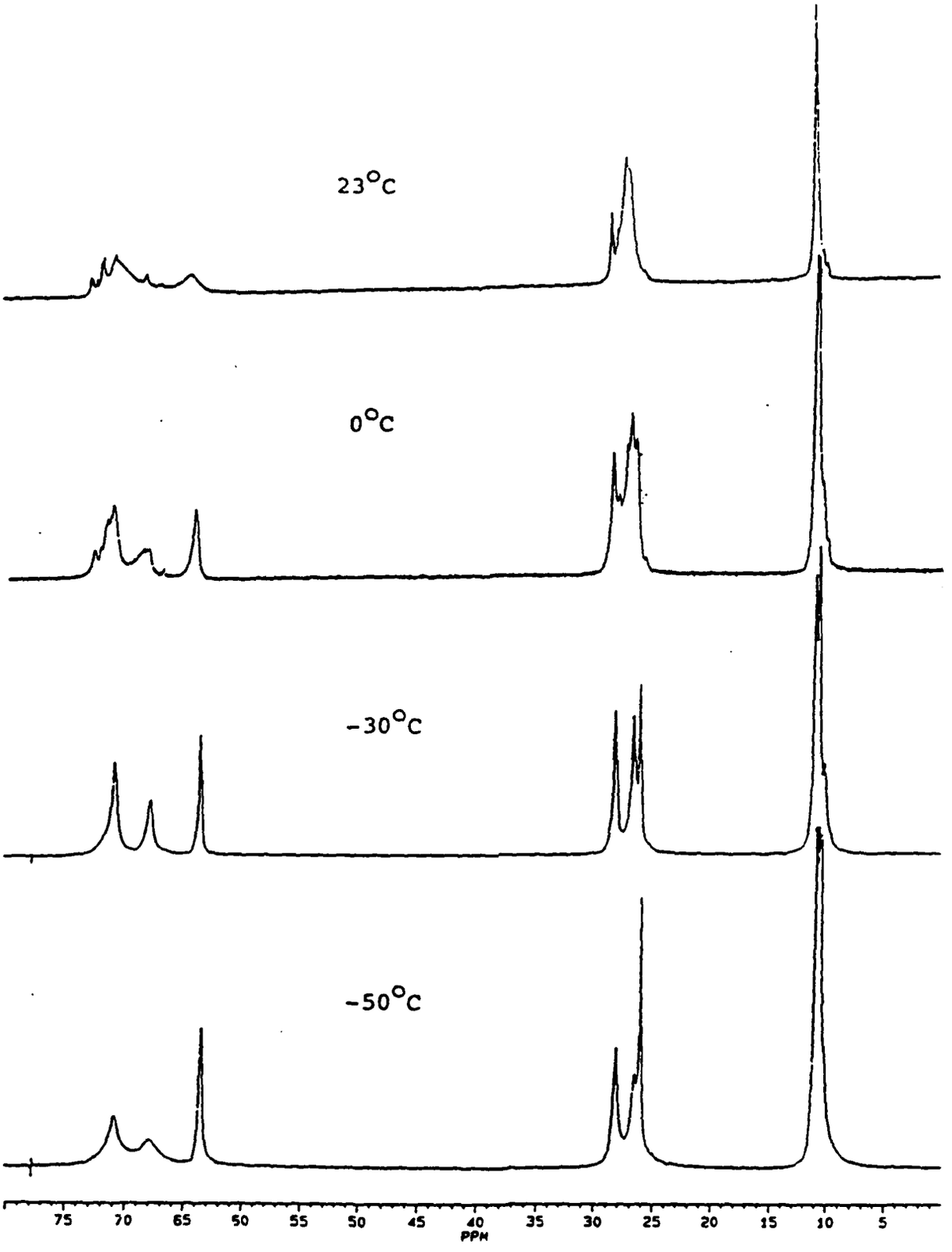


Fig. 12. ^{13}C NMR spectra for 34 mole% Zr n-propoxide in n-propanol at various temperatures.

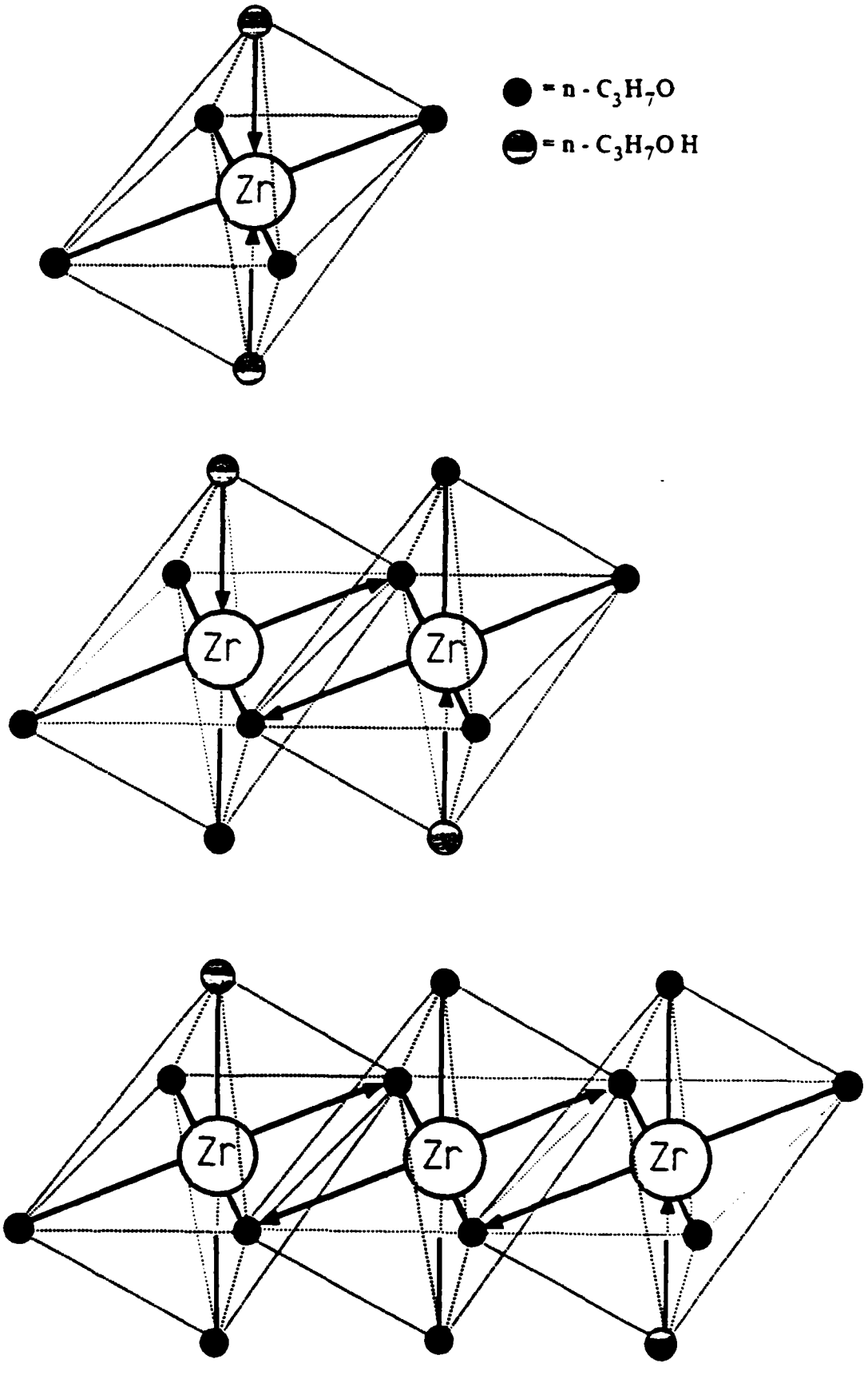


Fig. 13. Proposed structures of zirconium n-propoxide showing monomers and edge-sharing oligomers.

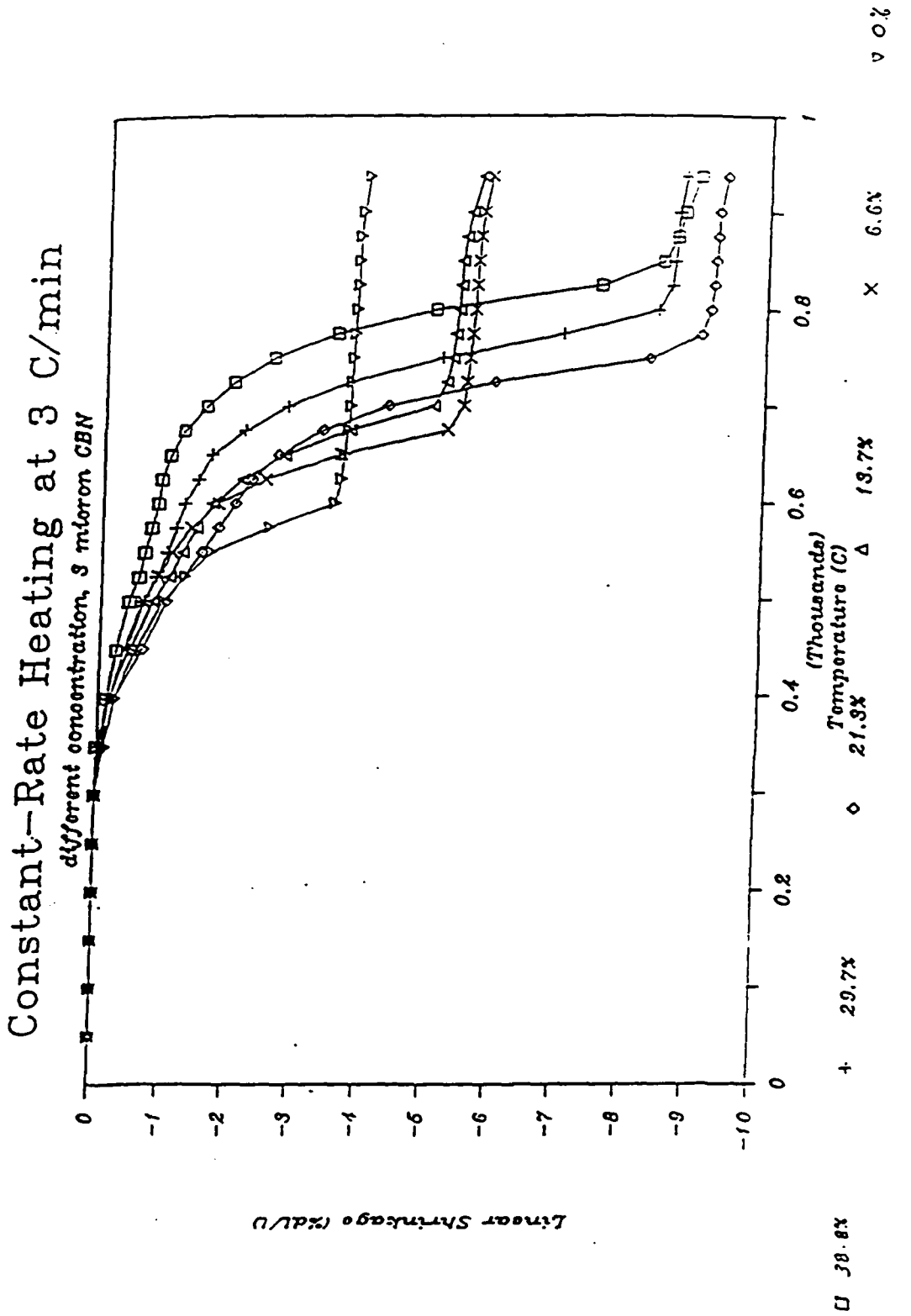


Fig. 14. Linear shrinkage vs. temperature for different cubic-BN volume %.

A second project involving basic studies of the sol-gel process was on the system Nd_2O_3-SiO_2. Because SiO_2 glass would be an excellent host for lasers using Nd ions, and because it is practically impossible to melt Nd_2O_3 into SiO_2 even at very high temperatures, the sol-gel process would be an apparently simple route. However, the question immediately arises as to the possibility of variations of the local environment of the Nd^{3+} ions in SiO_2 host and--hence, an alteration of their optical properties. During this period, a process was developed for the preparation of Nd_2O_3-SiO_2 glasses by the sol-gel process. Preliminary optical properties measurement suggest that at low concentrations, the local environment of the Nd^{3+} ion is six-coordinated as shown in Fig. 11. As the concentration of Nd_2O_3 increases, such an environment would become increasingly incompatible with that of a four-coordinated Si structure if Nd and Si shared oxygen neighbors. It is likely--then, that "phase separation" would occur, at least at $T > T_G$ of the glass. These possibilities are being investigated at present.

A third project involving basic studies of the sol-gel process was on the ZrO_2 system because of its fundamental difference from the SiO_2 system. This is caused by the difference in coordination numbers between Si and Zr. We have used high-resolution ^{13}C NMR to study the solution structure of zirconium n-propoxide in n-propanol. The spectra of a 34 mol% solution is shown in Fig. 12. From such studies, the structure of the zirconium alkoxides was determined. The proposed structure containing both edge and face-sharing octahedra is shown in Fig. 13.

e. Composites Derived from Gels

During this period we have concentrated our efforts on the SiO_2-cubic BN system. Cubic BN is as hard as diamond and composites with an oxide host should be very useful in many mechanical applications, as thick coatings or as monoliths like solid discs. Composites with up to 50% by volume of cubic BN have been successfully prepared via SiO_2 gel solutions. Although the BN dispersed phase is inert in SiO_2 gel solutions, we have found that the shrinkage behavior of the gel composite to be anomalous. Figure 14 illustrates such anomalous shrinkage behavior. It appears that the microstructure of the SiO_2 gel is significantly affected by the presence of the BN powder. A model is now being developed to explain this behavior.

3. Progress in Non-Oxide Glass Research

a. Chalcogenide Glass Fibers

During the course of our investigations of the structure of chalcogenide glasses, it was observed that even when fibers were prepared in a dry-box in dry N_2 and stored in the dry box (< 1 ppm H_2O and O_2), minute changes in the appearance of the surface of the fibers would occur. This led to a closer examination of the surfaces and the influence of ambient atmosphere and ambient radiation. We soon discovered that in the presence of UV, and even visible light, M-S and M-Se bonds were weakened or broken. Very small traces of O_2 would then react with the M atom to form an oxide. In the case of

As_2S_3 glass, for instance, As_2O_3 crystals were actually formed. This is shown in Fig. 15. As_2S_3 glass fibers, when exposed to weak UV and moist air, would readily form arsenic acid as shown in Fig. 16. The mechanical strengths of the chalcogenide fibers would then deteriorate rapidly. In total darkness, even an ambient atmosphere of 100% relative humidity did not lead to the formation of the oxide or the acid. These findings are important to the use of chalcogenide fibers for IR-transmission applications.

b. Chalcohalide Glasses

During this period, we have continued our research on the structure of these glasses. Work on the Ge-S-Br system was concluded, and work almost concluded on the Ge-S-I system. A complete assignment of the Raman bands for the Ge-S-Br system is shown in Table 2. Raman spectra of the Ge-S-I glasses, as the Ge:S ratio changes, are shown in Figs. 17 and 18. It appears that the structural variations are somewhat similar to that observed for the Ge-S-Br glasses.

c. Viscoelasticity of Fluoride Glass Fibers

We have reported that fluoride glass fibers, such as those of the Zr-Ba-La-Al type, can exhibit significant volumetric deformation at temperatures some 200°C below T_G. The activation energy for such low-temperature deformation is of the order of 10 Kcal/mole versus the values of > 50 Kcal/mole for viscous flow at above T_G and ~100 Kcal/mole near T_G. This is partially due to the excess free volume of the fibers because of rapid cooling. This research has now been concluded. A careful theoretical analysis suggest that this large deformation at low temperatures with low activation energies is most likely related to the entanglement of chain-like structural units, as reported for oxide glasses. No breakages of M-F bonds are involved nor is the process governed by the ionic transport of Fions. This research was presented at the XV International Glass Congress in July, 1989 in Leningrad, U.S.S.R.

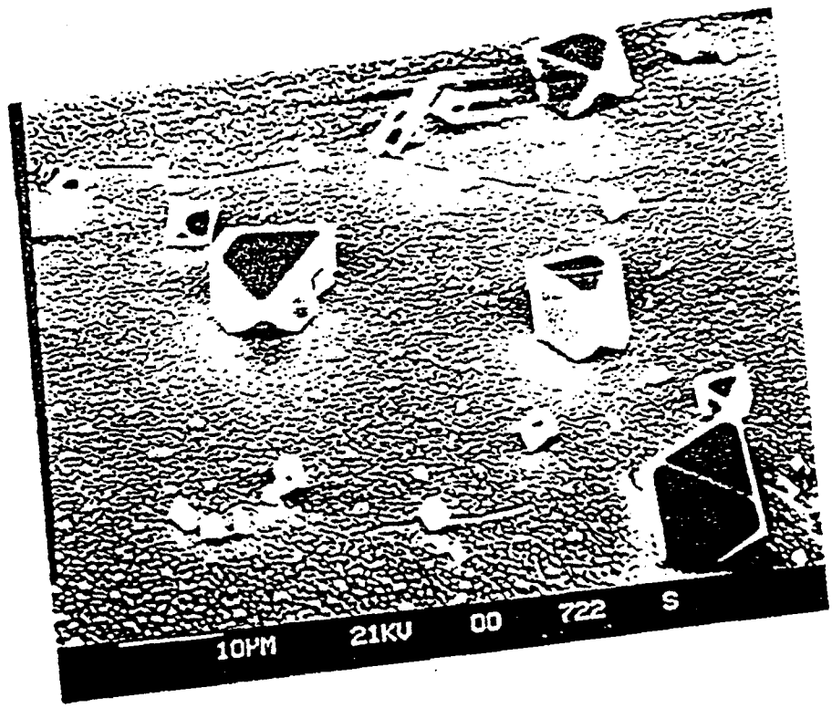


Fig. 15. Formation of As_2O_3 crystals on the surface of As_2S_3 glass after 24 hrs. in dry air exposed to a long wavelength UV lamp.

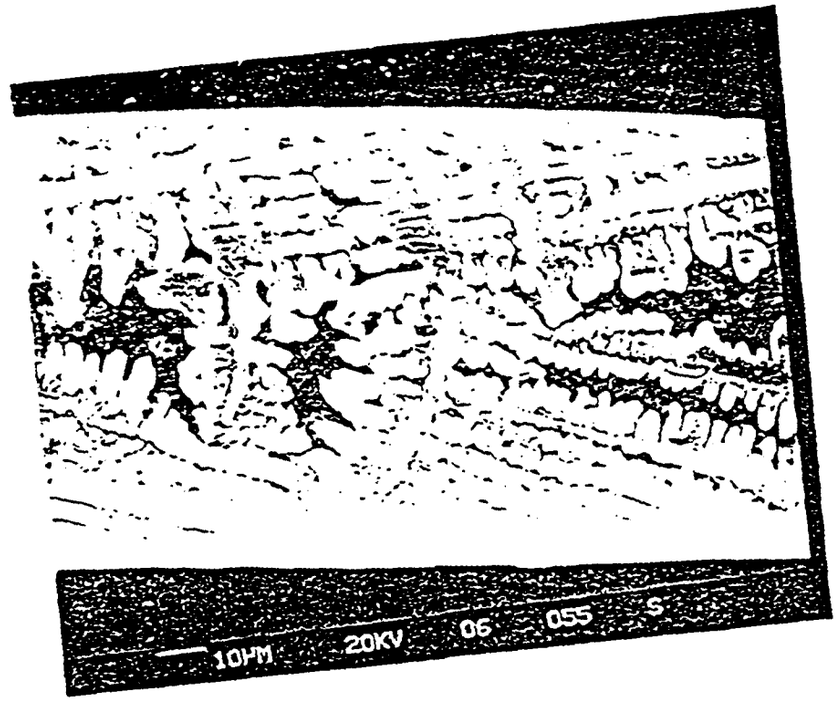


Fig. 16 Formation of arsenic acid on As_2S_3 glass fibers after 30 days in air and weak UV radiation.

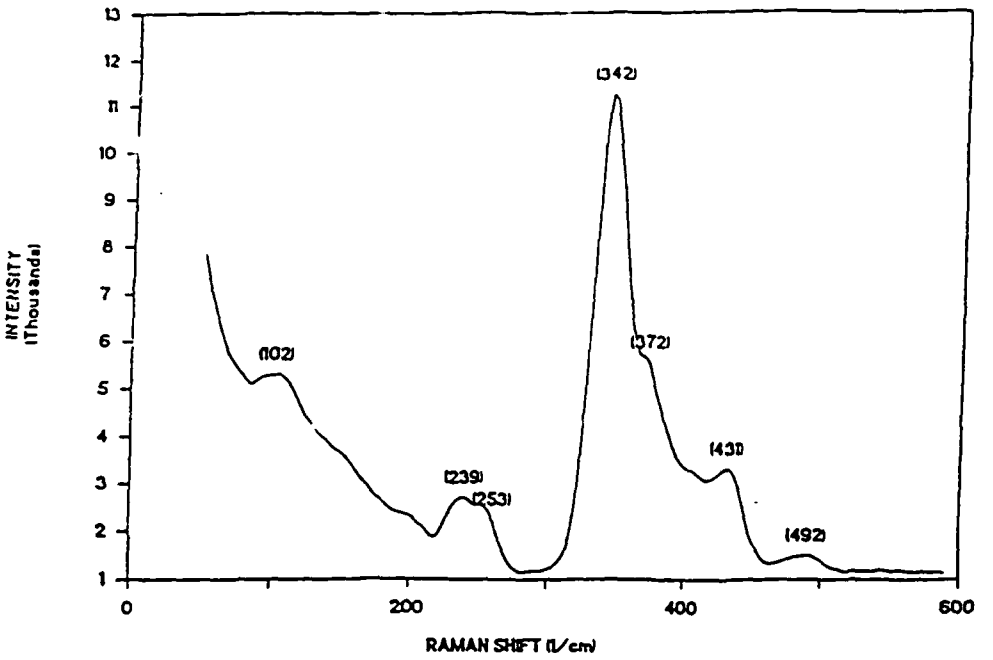


Fig. 17. Raman spectrum of $Ge_{32}S_{63}I_5$ glass.

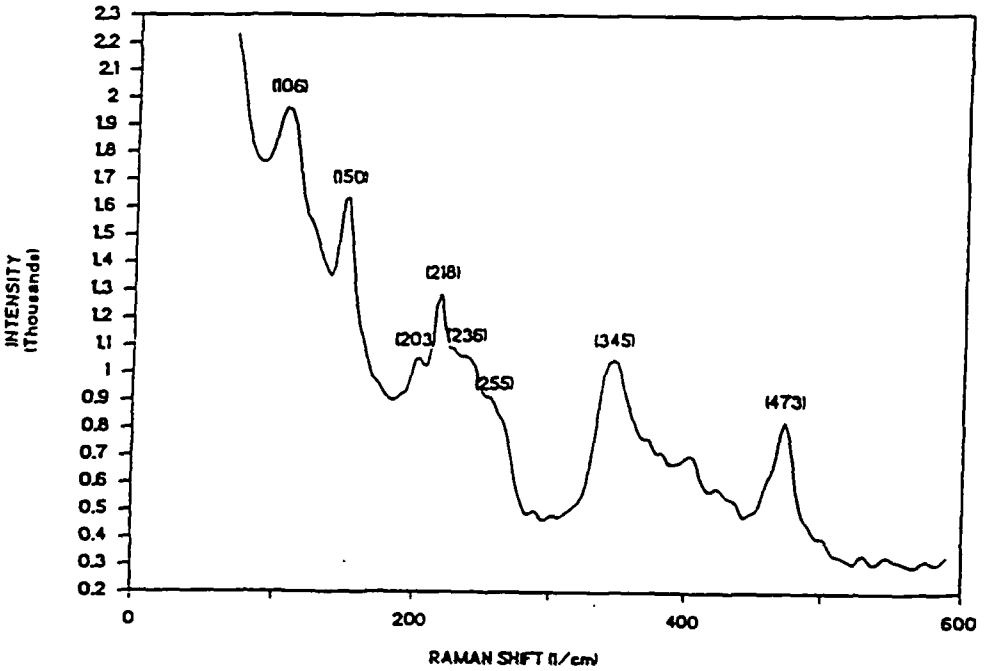


Fig. 18. Raman spectrum of $Ge_{21}S_{64}I_{15}$ glass.

Table 2. Frequency and assignment of the Raman bands in Ge-S-Br glasses

Frequency (cm^{-1})	Assignments
130	SD Ge-Br_3 (in $GeBr_3S$)
152	S_8(E2)
220	S_8(A1)
233	SS $GeBr_4$
254	SS Ge-Br (in $GeBr_2S_2$ and $BeBr_3S$)
264	SS Ge-Br (in $GeBrS_3$)
288	As Ge-Br (in $GBeBr_2S_2$)
300	As Ge-Br (in $GeBr_3S$)
342	SS GeS_4
375	GeS_4 edge-shared
475	S_8(A1) and Sn

SD - symmetrical deformation
SS - symmetrical stretching
AS - asymmetrical stretching

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300	As Ge-Br (in $GeBr_3S$)
342	SS GeS_4
375	GeS_4 edge-shared
475	S_8(A1) and Sn

SD - symmetrical deformation
SS - symmetrical stretching
AS - asymmetrical stretching

4. Cumulative Publications from this Grant

1. Mackenzie, J.D., "Chloride, Bromide and Iodide Glasses," NATO ASI Series 123, **Halide Glasses for Infrared Fiberoptics**, R.M. Almeida (ed.), Martinus Nijhoff Publishers, Dordrecht, (1987) p. 357.

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5. Educational and Professional Achievements

A great deal of the research performed on the AFOSR-funded project has been performed by undergraduate and graduate students as laboratory assistants and research assistants. During this period from November, 1987 to October, 1990, a number of students had received their M.S. and Ph.D. degrees through research partially performed under AFOSR support. Thus this research grant has been invaluable in its educational impact. The majority of the graduate students are now employed in research in defense-oriented laboratories in this country.

a. *M.S. Degree Recipients*

A. Janah - June, 1988
A. Sugitani - June, 1988
A. Mouchon - September, 1988
E. Bescher - June, 1989
C.J. Chu - December, 1989
D. Reinker - December, 1989

b. *Ph.D. Degree Recipients*

K.C. Chen - March, 1989
J. Heo - March, 1989
S.Y. Ryou - March, 1989
A. Nazeri-Eshghi - October, 1989
T.J. Yuen - December, 1989
E.J.A. Pope - April, 1990

Professor J.D. Mackenzie was presented with the Senior Research Award of the American Society for Engineering Education in Portland, Oregon in June, 1988 for significant contributions in advancing the frontiers of knowledge on engineering materials.

Professor J.D. Mackenzie was selected by the Alcoa Foundation to receive a Science Support Grant in 1989 for "Most Innovative Research in Materials."

Professor J.D. Mackenzie was selected by UCLA to be the first Nippon Sheet Glass Professor of Materials Science, a newly endowed chair at UCLA, in January, 1990.

6. Personnel

During this period, the following people had participated and made contributions to the progress reported.

Professor J.D. Mackenzie	Principal Investigator
Dr. R. Almeida	Visiting Research Fellow
Dr. H. Nasu	Visiting Research Fellow
Dr. J.S. Sanghera	Postdoctoral Scholar
Dr. Xu Yuhuan	Postdoctoral Scholar
Dr. K. Chemseddine	Postdoctoral Scholar
Dr. F. Kirkbir	Postdoctoral Scholar
Dr. Florence Babonneau	Postdoctoral Scholar
Dr. H. Kozuka	Postdoctoral Scholar
Ms. Mary Colby	Research Assistant
Ms. Christine Kanazawa	Research Assistant
Ms. Azar Nazeri-Eshghi	Research Assistant
Mr. Ren Xu	Research Assistant
Mr. Edward Pope	Research Assistant
Mr. Eric Bescher	Research Assistant
Mr. Jong Heo	Research Assistant
Ms. Annick Mouchon	Research Assistant
Mr. Joseph Yuen	Research Assistant
Mr. Y.J. Chung	Research Assistant
Mr. K.C. Chen	Research Assistant
Mr. C.J. Chu	Research Assistant
Mr. S.Y. Ryou	Research Assistant
Mr. Ken Cheng	Research Assistant
Mr. H.X. Zheng	Research Assistant
Mr. C.J. Chen	Research Assistant
Mr. A. Sugitani	Research Assistant
Mr. A. Janah	Research Assistant

In addition, a number of undergraduate laboratory assistants were employed to assist in this research program.

7. References

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